Characterization of the surfaces of single-walled carbon nanotubes using alcohols and hydrocarbons: A pulse adsorption technique

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ABSTRACT

A pulse mass analyzer was used to study the vapor phase adsorption of organic compounds on single-walled carbon nanotubes and chemically modified /oxidized SWCNTs. The change in mass of a packed bed of adsorbent held at 200 °C was observed following the injection of a pulse of an organic compound from the series: ethanol, iso-propanol, cyclohexane, cyclohexene, benzene, or n-hexane. The relative strength of adsorption was obtained by the mass increase resulting from injection of the pulse and by the time required for desorption. This time was broken into the transit time to reach the end of the bed and the half-time for return from peak to baseline. Hexane was the most strongly held compound of the organic sequence. Oxidative purification of a raw nanotube sample lead to a less hydrophobic surface. The effect of the purification was reversed by thermolysis at 700 °C, which removed oxygenated functional groups and increased the affinity for hydrocarbons. The amorphous carbon associated with the raw nanotube sample is a strong adsorbent for hydrocarbons. By comparison, an activated carbon had a greater affinity for hydrocarbons than any of the nanotube samples.

KEYWORDS – carbon nanotubes, adsorption properties, activated carbon

1. Introduction

The unique structure of single-walled carbon nanotubes (SWCNTs) gives them a wide variety of unique properties. Many of the potential applications for nanotubes have been recently reviewed [1]. It is reasonable that the porosity and pore structure of these materials could be the basis for their application as adsorbents, catalyst supports, and related materials. These pursuits may be assisted by more detailed information on the nature of the surface of SWCNTs. The study of the adsorption of gases on SWCNTs is an important means of probing the surface properties of these new materials. One important aspect of nanotube structure is the variety of possible sites available for adsorption [2]. The internal volume is more or less available depending on the degree to which the tubes have been opened. The propensity of nanotubes to bundle into ropes makes it necessary to consider additional sites that might be available. From simple consideration of ideal models of bundle structure the exterior sites would include interstitial channels between the tubes, the grooves found at the periphery of the bundles where tube exterior surfaces meet, and the outer curved surfaces of the exterior of the tubes were grooves can't be formed. In addition to these sites easily discerned from pictures of idealized nanotube bundles, the surfaces of the less regular carbons that are typical byproducts in many nanotube syntheses [3] must not be forgotten. The poorly defined impurities, amorphous carbons, and damaged nanotubes that commonly come along with nanotubes as they are prepared may be highly adsorbent materials in their own right.

In view of the possible complexity of the surfaces and the variety of materials that can be generated, it was thought worthwhile to develop a scheme to survey distinctive

features of the surface properties of nanotube samples [4]. In the following work, a picture of the surfaces of several nanotube samples is developed from two perspectives. First, their adsorption properties are compared with a related material, an activated carbon.   Second, comparison of the adsorption of members within a diverse set of compounds provides information about the nature of the interaction potentials found at the surface of the nanotubes. To gain a general picture of the surfaces of nanotube samples in this way, a systematic study was performed using a series of organic molecules consisting of hydrocarbons and alcohols. A sequence of organic compounds with similar heats of vaporization and boiling points but of different polarities and structures was specifically chosen. All of the work was done at a temperature well above the normal boiling point of the liquid probe molecules. Partial oxidation under carbon dioxide combined with a heat treatment was found to increase the hydrogen storage capacity of the nanotubes used here by a factor of three [5,6]. The effect of these treatments on the adsorption of the organic sequence is studied here to obtain more information on the changes that have occurred to their surfaces and to shed more light on the hydrogen storage results.

The method developed for this study made use of a pulse mass analyzer (PMA) [7]. The PMA is a versatile instrument that has been applied in wide variety of experiments. Studies of transient adsorption phenomena [8], coke deposition [9], the kinetics of reduction reactions [10], and adsorption isotherms [5,6,11] may be given as some examples. The experiments reported here illustrate another application, direct observation of rates of desorption made by use of a pulse technique. In this work, a pulse was formed by the injection of the probe molecule into the preheated (200 °C) carrier

gas. The pulse was then swept through a packed bed of the adsorbent. The mass change

of the packed bed is recorded with time resolution on the order of tenths of a second. The

peak height, transit time, and desorption decay curve from each injection were used to

measure the adsorption properties.

2. Experimental

2.1 *Instrumental*

A diagram of the pulse mass analyzer (PMA) is given in Figure 1. The instrument

(TEOM series 1500 Pulse Mass Analyzer manufactured by Rupprecht and Patashnick,

Albany NY) is a flow-through microbalance that detects mass changes by an inertial

system. It employs a vibrating tapered glass element to measure mass changes. The

element consists of a hollow glass tube that leads the gas stream through a cylindrical

sample bed, diameter 4 mm, height 6 mm, located at its lower end.   Samples were

packed into the bed between "Astro quartz" wool plugs and retained there by a ventilated,

gold-plated metal cap.   Gas streams were controlled using a manifold that included mass

flow controllers and a back-pressure regulator. Instrument control and data recording

were managed through a PC system utilizing Labview$^{©}$ software programmed to control

and record valve positions, the selection of the gases, their flow rates, system pressure

and temperature, and other functions. Two gas streams were supplied to the instrument

through mass flow controllers; one passes through the sample in the packed bed (carrier

gas) and one sweeps the volume outside the sample bed (purge gas). Organic compounds

were injected into the heated carrier gas stream through a septum using a 1.0 or 10 μl

syringe. The tapered-element is enclosed within a heated stainless steel pressure vessel.

The instrument is capable of operating from ambient temperature to 700 °C and from

ambient pressure to 700 psia. The combined flow of both gas streams was sampled at the exit port by a capillary tube that serves as a transfer line to a quadrupole mass spectrometer (AMETEK MA 200).

The operating principle of the instrument is based on the change in the frequency of oscillation of the tapered element caused by a change in the mass of the sample bed. The element is stimulated to vibrate at its natural frequency (in the range of 40 cps) by a mechanical driver. The frequency of oscillation is measured by an optical system through two ports in the pressure vessel. Mass changes are determined by means of equation 1,

$$\triangle m = k/(1/f_1{}^2 - 1/f_2{}^2) \qquad (1)$$

where f_1 and f_2 represent the frequencies observed at two different times, and k is an empirically determined constant. To determine the value of k, the instrument was equilibrated at the temperature and flow conditions to be used. The vibrational frequency of the empty reactor was measured with and without the retaining cap in place. The constant was calculated using the known mass of the cap. Since k changes in a complex way with temperature, all of the data in this study were acquired under isothermal conditions.

The carrier gases, helium or nitrogen, were Matheson UHP grade (99.99 % or higher) and were passed through a Matheson Gas Purifier Cartridge Type 452 (4A molecular sieves) to remove traces of moisture.

2.2 *Sample Preparation*

2.2.1 *Carbon Samples*

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Nanotube samples were purchased from Tubes@ Rice in two different grades [12]. "Raw Material Grade", referred to as raw tubes, was obtained as a solid, fibrous mat. It was subjected to a mild grinding to make it easier to pack it into the sample holder. "Purified Grade", referred to as pure tubes, was obtained as a suspension in toluene. Typically, 15 ml of the well-shaken suspension was withdrawn and evaporated with a stream of dry nitrogen at room temperature. After the toluene had been removed the sample was dried at 140 °C for about 5 hours. About 90 mg of dry SWCNTs (pure tubes) were obtained by this procedure.

Carbon dioxide oxidized samples were prepared by a mild oxidation with carbon dioxide at ca. 600 °C. The SWCNT sample (75-125mg) sandwiched between quartz wool plugs was placed in a 20cm by 12mm OD Vycor tube and heated in a tube furnace to 600 °C under argon or helium flow (5ml/min). The exit gas was monitored by mass spectrometry. Once the temperature was reached carbon dioxide was added to the flow at 5ml/min making the total flow 10ml/min. The sample was kept under CO_2/inert gas flow until carbon monoxide levels dropped to baseline values. The sample was then cooled to room temperature under inert gas flow.

The "cut tubes" were prepared similar to Smalley et al. [13]. A sample of pure tubes was mixed with H_2SO_4/HNO_3 (3:1) and sonicated for several hours at 70 °C. After 2 to 3 hours the sample was filtered and washed well with water, then evaporated and dried in a vacuum oven for 4 to 5 hours prior to grinding. This process is believed to shorten tubes and create a more open nanotube structure.

A commercial grade of activated carbon, Norit, (Fisher Scientific) was dried at 200 °C prior to grinding and placement in the reactor.

2.2.2 *Adsorbates - the organic sequence*

All of the organic compounds used in this study were supplied as 99+% pure and used without further purification. The sequence (with BP) was: ethyl alcohol (78.5 °C), isopropyl alcohol (82.4 °C), cyclohexane (81.0 °C), cyclohexene (83.0 °C), benzene (80.1 °C), and n-hexane (68.0 °C).

3. **Results and Discussion**

3.1 *Organic Sequence – general*

The adsorption/desorption experiments were conducted with a standard protocol to allow direct comparison of the results. With the carbon sample packed in the fixed bed, the carrier and purge gas flow rates were each set at 50ml/min of helium. Sufficient time was allowed at the temperature set point prior to injection to permit the vibrational frequency of the instrument to regain a stable baseline. This required several hours for samples heated from ambient temperature to 200 °C, but only about one hour following thermal pretreatment at 700 °C (where employed). Individual injections of the organic liquids (1.0 μl) were made by syringe into the heated injector port (200 °C). The organic vapor was carried to the fixed bed of adsorbent within 1-2 seconds. Without a sample in the fixed bed only a small deflection from the baseline mass (ca. 10-20 μg) was observed and the return to the baseline was almost immediate (1 sec). This relatively small deflection reflects the minor change in carrier gas density caused by the pulse of organic vapor. With a sample present, the adsorption event was revealed by a rapid rise in mass followed by a slower return to baseline as desorption took place. A typical experiment is shown in Figure 2 for duplicate injections of each organic compound. Each peak represents a single 1.0 μl injection of the selected organic compound.

3.2 *Organic Sequence – analysis of peak heights*

Adsorption of the organic compounds by the packed bed was evaluated by comparing the weight of material that was retained from the standard 1.0 μl injections. The peak heights are given in Table 1 for nominally 50 mg samples of two different adsorbents that had been pretreated at 200 °C or 700 °C. The portion of each injection adsorbed ranged from 17% to essentially 100%. The amount adsorbed is also given in terms of millimoles of adsorbate per gram of carbon adsorbent (mmole/g) and the number of micromoles of adsorbate per square meter of carbon adsorbent (μmole/m^2). The total amount adsorbed depends on the nature of adsorbent and the adsorbate as well as the pretreatment temperature and surface area. The hydrocarbons - cyclohexane, cyclohexene, benzene, and n- hexane - were each completely retained on Norit after either pretreatment temperature (allowing for an approximate 10% experimental error). The adsorption of the two alcohols on Norit was less effective in both cases. For example, only 37% of ethanol and 57% of isopropyl alcohol were adsorbed on Norit pretreated at 700 °C.

In general, the pure tubes did not adsorb as much material as the Norit. None of the injections on pure tubes was completely adsorbed. Of all the samples investigated, only pure tubes pretreated at 200 °C showed a preference for alcohols over hydrocarbons. The affinity of alcohols for oxygenate functional groups on the surface of purified SWCNTs has recently been demonstrated [14]. Analysis of isotherms for ethanol and methanol led to the conclusion that ethanol adsorption at low relative pressure depends on the polarity of the surface. This work makes clear that both access to the micro-porosity of nanotubes and the polarity of the micro-pore surface are changed by oxidative

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purification [14]. This increase in polarity can be reversed by thermal dissociation of the functional groups. Although the pretreatment at 200 °C is likely to remove just volatile contaminants adsorbed during prior exposure to the atmosphere, thermolysis at 700 °C induces breakage of chemical bonds. Loss of oxygenated functionality was confirmed by observation of an increase in the signals for CO and CO_2 in the exit gas by mass spectrometry during the course of heating to 700 °C. The loss of surface groups induced by heating above 350 °C has been reported for a sample of nanotubes similar to those used here [15]. Approximately 5% of the carbon atoms were found to be located at readily oxidized defect sites [16] and their removal is thought to increase access to the interior of the nanotubes [18]. Because of this alteration in surface chemistry it is interesting to compare the effect of pretreatment temperature on the two samples.

By comparing the results obtained before and after heating to 700 °C, it is evident that both samples have become more hydophobic as a result of loss of oxygenated groups. For Norit, the selectivity for hydrocarbons over alcohols became more distinct principally because it lost some ability to adsorb the alcohols. The trend is similar for pure tubes, but the selectivity actually inverts. Instead of favoring alcohols over hydrocarbons, the sample now favors hydrocarbons over alcohols. The amount of ethanol adsorbed decreased by almost a factor of three and that of isopropyl alcohol by a lesser amount. Also, in absolute terms more of the hydrocarbons and less of the alcohols were adsorbed after pretreatment to 700 °C.

The amounts adsorbed are also compared in Table 1 on the basis of millimole organic compound per gram adsorbent. This gives a measure of loading on the

adsorbent. In every case, the number of millimoles of organic compound adsorbed per gram sample is higher for Norit than for the pure SWCNTs.

The last column in Table 1 gives a comparison taking into account the surface areas. Due to the more than two-fold difference in surface area, coverages of the pure sample are close to or even exceed those of Norit in spite of the fact it takes up lesser absolute amounts. From the data taken after heating at 200 °C, similar coverages of hydrocarbons were found for Norit (0.31-0.41 μmoles/m^2) and pure tubes (0.28-0.38 μmoles/m^2). For the alcohols, the coverage of pure sample (0.52-0.70 μmoles/m^2) is somewhat larger than that for Norit (0.45-0.47 μmoles/m^2).

The surface areas listed in Table 4 were determined for samples before they were loaded into the reactor. As part of the surface area analysis routine, they were first baked out at 150 °C at low pressure for 12 hr. However, interpretation of the coverage of samples after they have been taken to 700 °C must be done with caution. It has been reported that the functional groups left behind by the oxidative purification process can block entry to the micropores of SWCNTs [17]. Further, annealing a sample of purified tubes at 1073 K has been shown to open up the interior to the adsorption of argon [18]. The monolayer coverage of argon was estimated to be 3 mmole/g. In our case, almost assuredly the surface areas have changed during thermolysis at 700 °C, and probably increased due to the loss of blocking groups.

Despite a degree of uncertainty in the coverages found after treatment at 700 °C, it still is of value to make comparisons to estimates for monolayer coverage based on the BET results. From this data, the monolayer coverages of nitrogen on Norit and pure tubes are 5.5 and 2.2 mmole/g, respectively. This is at least twenty times the loading

found for the organic adsorbates. The surface area taken up by the large and complex

organic molecules on the irregular carbon surfaces is not known. However, even if the

organic molecules require an order of magnitude more area than nitrogen, it is still

evident that at most only a fraction of a monolayer is occupied. The relatively high

temperature of our measurements (200 °C) must also considered in this regard. The

vapor pressure of each of the adsorbates estimated at this temperature by extrapolation of

thermodynamic data range from 14.4 to 29.7 atm. The peak pressure of the transient

pulse can be no more than slightly above one atm. Thus the maximum reduced pressures

produced by a pulse would range roughly from 0.07 to 0.03. Capillary condensation is

not likely to be a factor under these conditions.

From the standpoint of the amounts adsorbed, heat treatment to 700 °C appears to

alter the surface, especially to the detriment of the adsorption of polar compounds. The

sample of pure tubes took up greater amounts of the hydrocarbons but lesser amounts of

the alcohols. Thus, even though more of the interior area of the sample may have

become available after heat treatment, the loss of oxygen functional groups has rendered

the surface less able to retain the hydrophilic compounds. The changes in surface

properties are more clearly defined when the desorption times are compared. Norit took

up the entire amount of each of the hydrocarbons injected after either pretreatment

temperature.

3.3 *Organic Sequence - analysis of desorption times*

Desorption curves for the pure tubes heated to 700 °C are given in Figure 2 where

duplicate injections of the six compounds of the organic sequence are plotted. The

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curves have a complex shape that cannot be represented by a single first-order decay process. In general, the desorption curves are a mixture of relatively rapidly and slowly desorbing components. Evidently, the SWCNTs have several kinds of adsorption sites with different affinities for the organic compounds. The relative strength of the adsorption was judged from two time features taken from the decay curves. Different peak shapes were observed depending on the degree of retention. For many cases the peak reached a maximum and began to decay immediately. However, for several injections on the Norit sample in which 100 % of the material was adsorbed, a somewhat different peak shape was observed as shown in Figure 3. The mass rose, reached a value corresponding to the total sample weight injected, and then formed a plateau before eventually beginning to fall. The length of this plateau is related to the time required for the "front" of the adsorbate to pass through the bed. This time is referred to as the transit time (TT) in Tables 2 and 3. Once the adsorbate front reached the end of the bed the recorded mass started to decrease and the desorption curve was established. The half-life of the decay was measured from the end of the plateau to the point where one half of the original mass had desorbed. This time is called the half-width or Width in Tables 2 and 3. The third column in Tables 2 and 3 is the total of these two times. The more strongly adsorbed materials had longer transit times (TT) and longer decay times (Width). For those materials that did not adsorb strongly enough to render a measurable transit time, the half-width measurement alone provides a value for making a relative comparison of the strength of adsorption.

3.3.1 *Desorption from samples before thermolysis*

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Table 2 compares the decay times for two samples of nanotubes and Norit after pretreatment at 200 °C. The largest span in total time was observed for the Norit sample. The comparatively short times for desorption of the alcohols versus the hydrocarbons indicate a relatively hydrophobic character of the surface. A robust discrimination among the hydrocarbons is also found. The linear alkane, hexane, is much more strongly held than its cyclic analog. Among the six-membered ring compounds there was a steady progression toward longer times as the number of pi bonds (the degree of unsaturation) increased. Thus both shape and functionality play major roles in determining the relative affinity for members of this series.

The pure tubes show a markedly lower affinity for the hydrocarbons in comparison to the activated carbon. First, the transit time (TT) is zero for all members of the organic sequence. In fact, the half-widths for the decay (Width) of all the compounds are nearly the same. The surface of the pure tubes is not well differentiated by this series of compounds as it adsorbs both polar and non-polar species weakly.

The adsorption strength of the raw tubes across the whole organic sequence is much greater than that of the pure tubes but still less than that for the activated carbon. The raw tube sample contains a large fraction of amorphous carbon along with nanotubes. This amorphous carbon evidently has a high surface area because removal of this fraction on going from raw to pure tubes substantially reduces the BET value (Table 4). The amorphous carbon may well be primarily responsible for the relatively strong adsorption found for the raw tubes.

3.3.2 *Desorption from samples after thermolysis*

The half-widths for decays obtained after the samples had been heated to 700 °C are shown in Table 3. This table includes the three samples previously examined at 200 °C plus two samples of pure tubes that have received further oxidative treatment. For every sample the evolution of CO, CO_2, and trace amounts of H_2O was observed in the exit gas stream by the mass spectrometer during the course of heating to 700 °C under helium. Loss of this type of functionality would be expected to generate a less polar or more hydrophobic surface. This is borne out by comparison of Table 2 and 3. After heating to 700 °C there was an increase in the decay times for all the hydrocarbon species on each of the samples. There was little or no change for the alcohols.

The measured half-widths (Width) and total times (TT + Width) for the Norit sample show that its selectivity toward hydrocarbons remained about the same after heating. The relative difference between cyclohexane and cyclohexene is somewhat larger, but the general order has not changed.

By comparison, larger differences are found for the pure and raw nanotubes. The strength of hydrocarbon adsorption on the raw tubes was substantially increased upon treatment to 700 °C. The raw tubes developed the greatest affinity for the hydrocarbons of all the SWCNT samples studied. A significant degree of selectivity is also found. Hexane, in particular, showed the largest increase, and is held much more strongly than any of the cyclic structures. In general, the decay times are within one half to two thirds of those found for Norit. It is of note that benzene is not held as long as cyclohexene, the reverse of the order found with Norit.

The four nanotube samples of Table 3 represent different degrees of oxidation/purification treatment beginning with raw material. Pure tubes were made by

oxidation of raw material with nitric acid [19]. This process removes most the amorphous carbon. Further modification of the pure tubes was accomplished in our laboratory by two different oxidative procedures; (1) the nitric acid/sulfuric acid oxidation with sonication to prepare cut tubes [13] and (2) the carbon dioxide oxidation at 600 °C [20]. The former procedure is reported to shorten the average length of the tubes and open capped ends [13]. All of the samples in Table 3 have been pretreated to 700 °C with one exception. The CO_2 oxidized sample was prepared at 600 °C, but was not heated to the higher temperature in the pulse mass analyzer.

The data of Table 3 clearly show a progression in the adsorption patterns as a function of oxidation of the raw tubes. First, none of the samples has a great affinity for the alcohols. As mentioned above, this is probably due to the removal of polar functional groups by pretreatment at 700 °C. Each of the samples retains the hydrocarbons to a greater degree than the alcohols and here significant differences are observed.

In parallel with the results found earlier after the pretreatment at 200 °C (Table 2), raw tubes definitely have the highest affinity for hydrocarbons. Oxidative removal of the amorphous material results in a marked decrease in the strength of adsorption of the hydrocarbons. This again points to the fact that in the raw tubes amorphous carbon may dominate the adsorption properties. Further comparison with the 200 °C data again shows that loss of functional groups has increased the selectivity of the raw tubes. The pyrolysis also changes the surface of the pure tubes to one that discriminates between hydrocarbons and alcohols.

Further oxidation of pure tubes produced the cut tube sample. The cut tubes show a very modest change in adsorption as a result of this oxidative treatment. The oxidative

cutting action of the nitric acid/sulfuric acid process is similar but somewhat more severe than that used to produce the pure tubes in the first place, and apparently does little to change the adsorption properties. Evidently the further oxidation of tubes obtained by the cutting procedure has little effect on the strength of adsorption.

Significant changes were observed when the pure sample was oxidized with CO_2 at 600 °C. The half-widths for the hydrocarbons were roughly doubled. Further, hexane now has a significant transit time as well. The CO_2 oxidized sample has the greatest adsorption strength of all the purified nanotubes. Only the raw tubes containing the large component of amorphous carbon show stronger adsorption. The CO_2 oxidation procedure has been shown to be effective for activation of these samples for hydrogen adsorption as well [5,6]. In that case the capacity to store hydrogen at 700 psia was found to be about triple that of either pure or raw tubes. The root cause of the increase in hydrogen capacity and the increase in strength of hydrocarbon adsorption may be the same.

4. Conclusions

We have demonstrated the use of the Pulse Mass Analyzer as a primary tool in the investigation of the adsorptive/desorptive properties of carbon nanotubes and related carbon species. The pulse/injection method provides data on both the amount of adsorbate taken up and the rate of its desorption. This quantitative study shows that the amount taken up by a packed bed of adsorbent from a pulse of an organic compound injected into a flowing carrier gas can be directly measured at a chosen isothermal condition. The adsorption profiles are reproducible and can be measured with a good degree of accuracy. The desorption curves for all of the nanotubes investigated were

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complex and consistent with surfaces of considerable heterogeneity of adsorption strengths. This result fits an emerging pattern of adsorption behavior on nanotubes. For example, the isosteric heats of adsorption of Ar [18], Xe [21], and methane [22] on nanotubes also have been reported to be a function of coverage.

A relative average "adsorptive strength" was determined by using the half-width of the decay curve and in some cases the transit times. The values were compared among a series of alcohols and hydrocarbons of roughly equivalent boiling point. This sequence probes the character of the surface in terms of its relative hydrophilicity and its preference for saturated versus aromatic compounds. Thus, a methodology for surveying the adsorption properties of carbon nanotubes was established based on the relative amounts adsorbed and the times required for desorption.

The organic compounds used in this study clearly differentiate these carbons according to the gross nature of their surfaces. Norit and raw tubes are clearly hydrophobic as demonstrated by a strong preference for adsorption of the hydrocarbons over alcohols. As estimated from the desorption times, all of the SWCNT samples have a smaller interaction potential toward hydrocarbons when compared to the activated carbon. Oxidation of raw tubes to produce pure tubes resulted in the selective loss of amorphous carbon. This reduced both the surface area of the sample and the average strength of adsorption of the hydrocarbon compounds. This oxidative treatment not only removes amorphous carbon but also increases the oxygen content by a considerable amount (raw - 4.9% oxygen, pure -13.3% oxygen). Pure tubes do not show a marked discrimination between alcohols and hydrocarbons in contrast to the raw tubes. The oxidation has apparently compromised the hydrophobic nature of the surface. This

condition is reversed by thermolysis at 700 °C, which removes functional groups. After thermolysis the coverages obtained by a pulse of the hydrocarbons became greater than those from the alcohols. The desorption times for the hydrocarbons were also increased.

A further oxidation of pure tubes with sulfuric acid/nitric acid did little to improve the adsorptive strength for hydrocarbons. The increase in dispersion thought to be obtained by the cutting procedure had, at best, a modest effect on adsorption strength.

Activation of the pure sample by CO_2 oxidation was more effective in enhancing the interaction potential with hydrocarbons. Except for the raw tubes, which contain abundant amorphous carbon, the CO_2 oxidized pure sample is the best material for adsorption of hydrocarbons of the nanotube samples investigated here.

Further work is in progress to examine other aspects of SWCNT structure by using the pulse adsorption technique. Preliminary work shows that adsorption strength is a strong function of the functional groups of the adsorbate molecules and also to some degree the shape of the adsorbate molecule.

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Disclaimer

Reference in this work to any specific commercial product is to facilitate understanding and does not necessarily imply endorsement by the United States Department of Energy.

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TABLE 1. Peak Heights from injections on Norit and Pure Nanotubes pretreated at 200 °C and 700 °C.

Norit – 700 C	peak height mg	mg injected	% of injection absorbed	mmole/g sample	μmoles/m^2
Ethanol	0.29	0.78	37	0.12	0.23
2-propanol	0.44	0.78	57	0.14	0.26
Cyclohexane	0.79	0.78	101	0.18	0.34
Cyclohexene	0.83	0.81	102	0.19	0.36
Benzene	0.85	0.88	97	0.21	0.38
n-hexane	0.73	0.66	111	0.16	0.31
Pure tubes– 700 C					
Ethanol	0.14	0.78	17	0.05	0.23
2-propanol	0.25	0.78	32	0.08	0.38
Cyclohexane	0.46	0.78	59	0.10	0.47
Cyclohexene	0.58	0.81	71	0.13	0.61
Benzene	0.62	0.88	70	0.14	0.66
n-hexane	0.55	0.66	84	0.12	0.56
Norit – 200 C					
Ethanol	0.57	0.78	73	0.24	0.45
2-propanol	0.77	0.78	98	0.25	0.47
Cyclohexane	0.80	0.78	103	0.18	0.34
Cyclohexene	0.83	0.81	102	0.19	0.36
Benzene	0.89	0.88	101	0.22	0.41
n-hexane	0.71	0.66	108	0.16	0.31
Pure tubes – 200 C					
Ethanol	0.37	0.78	47	0.15	0.70
2-propanol	0.35	0.78	45	0.11	0.52
Cyclohexane	0.26	0.78	33	0.06	0.28
Cyclohexene	0.25	0.81	31	0.06	0.28
Benzene	0.33	0.88	38	0.08	0.38
n-hexane	0.28	0.66	43	0.06	0.28

TABLE 2. Transit times and Peak widths for nanotube samples and Norit pretreated at 200 °C. Time in seconds.

Pretreat 200 C	Norit			Raw Tubes			Pure Tubes		
	TT	Width	Total	TT	Width	Total	TT	Width	Total
Ethanol	0	10	10	0	13	13	0	14	14
2-propanol	0	15	15	0	13	13	0	17	17
Cyclohexane	2	67	69	0	34	34	0	17	17
Cyclohexene	16	96	112	9	52	61	0	19	19
Benzene	35	158	193	11	54	65	0	20	20
n-hexane	49	215	264	24	122	146	0	20	20

TABLE 3. Transit times and Peak widths for nanotube samples and Norit pretreated at 700 °C. Time in seconds.

Pretreat 700 C	Norit			Raw Tubes			Pure Tubes			Cut Tubes			CO2 Ox Pure Tubes		
	TT	Width	Total	TT	Width	Total	TT	Width	Total	TT	Width	Total	TT	Width	Total
Ethanol	0	10	10	0	12	12	0	10	10	0	11	11	0	14	14
2-propanol	0	13	13	0	12	12	0	14	14	0	14	14	0	19	19
Cyclohexane	13	72	85	10	45	55	0	39	39	0	40	40	0	66	66
Cyclohexene	28	145	173	17	91	108	0	35	35	0	54	54	0	73	73
Benzene	47	197	244	8	72	80	0	43	43	0	48	48	6	66	72
n-hexane	106	324	430	46	216	262	0	68	68	0	87	87	24	174	198

TABLE 4.   BET Surface Areas and Oxygen Determination.

	Norit	Pure Tubes	Raw Tubes	CO2 Ox Pure Tubes
BET Surface area (m^2/g)	533	213	358	189
Oxygen wt%	10.3	13.3	4.9	8.0

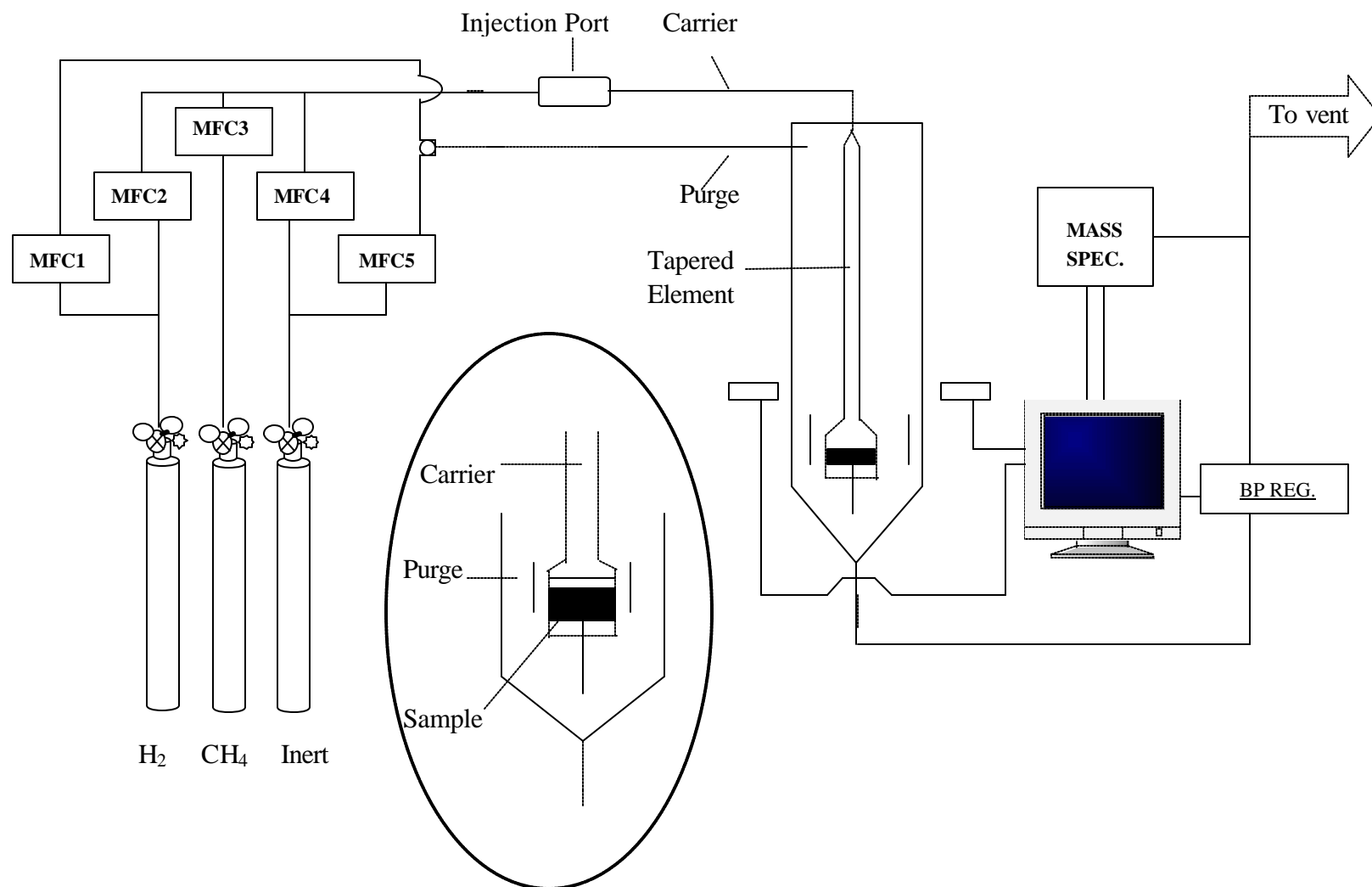Figure 1. Flow diagram of TEOM 1500 pulse mass analyzer.

Figure 2. Duplicate injections of the Organic Sequence on Pure Tubes Pretreated at 700 °C.
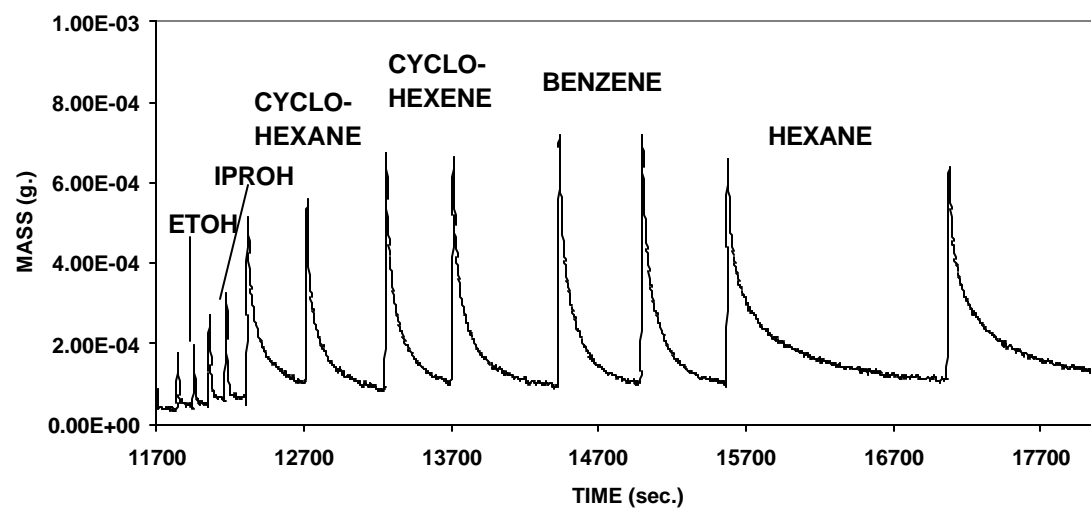

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Figure 3. Analysis of Transit Time (TT) and Decay Time (Width) for Benzene on Norit at 700 °C.